Seasonal Variations of Water Vapor in the Lower Stratosphere Inferred from ATMOS/ATLAS-3 Measurements of H_2O and CH_4

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Abstract. Stratospheric measurements of H_2O and CH_4 by the. Atmospheric Trace Molecule Spectroscopy (ATMOS) Fourier transform spectrometer on the ATLAS-3 Shuttle flight in November 1994 have been examined to investigate the altitude and geographic variability of H_2O and the quantity $H = (H_2O + 2CH_4)$ in the tropics and at mid-latitudes (8-49°N) in the northern hemisphere. The measurements indicate an average value of 7.18 ± 0.43 ppmv for total hydrogen H between altitudes of about 18 to 35 km, corresponding to an average water vapor mixing ratio of 3.81±0.29 ppmv entering the stratosphere. The H_2O vertical distribution in the tropics exhibits a wave-like structure in the 16-25 km altitude range suggestive of seasonal variations in the water vapor transported from the troposphere to the stratosphere. The hygropause appears to be within ~2 km of the tropopause, with the vertical resolution limited try the field-of-view of the ATMOS measurements. This is consistent with the phase of the seasonal cycle of H_2O in the lower stratosphere, since the ATMOS observations were made during the time period when the H_2O content of air injected into the stratosphere from the troposphere is relative low.

introduction

The stratospheric water vapor distribution is determined by a combination of chemical and dynamical processes. Chemical processes involving the oxidation of CH_4 enhance the abundance of H_2O, producing approximately two molecules of H_2O for each molecule of CH_4 and leading to higher H_2O mixing ratios with altitude. Since H_2O is a major source of the reactive odd hydrogen species, and is considered to be an important tracer of transport from the troposphere to the stratosphere, measurements of its stratospheric distribution have been extensive and have been carried out with a variety of techniques including ground-based, and aircraft-, balloon-, and satellite-borne instruments (e.g., Hansen and Robinson, 1994; Gunson et al., 1990; McCormick et al., 1993; Oltmans and Hofmann, 1995).

The ATMOS/ATLAS-3 limb viewing solar occultation observations of stratospheric trace constituents provide simultaneous measurements of H_2O and CH_4 distributions over the 8-49°N and 67-72% latitude ranges during 3-12 November 1994 (Gunson et al., 1996). This paper focuses on a portion of the retrieved data for the

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16-35 km altitude range at northern mid-latitudes and tropics, We test the conservation of effective total hydrogen $H = (H_2O + 2CH_4)$, deduce the average H_2O mixing ratio transported to the stratosphere, and examine profiles of H for evidence of seasonal variation of water vapor entering into the stratosphere.

Methane Oxidation and the Hydrogen Budget of the Lower and Middle Stratosphere

Methane is oxidized in the stratosphere mainly by reactions with OH and $O(^1D)$ and to a lesser extent Cl. 'The net result of a series of reactions leads to formation of approximately two molecules of H_2O for each molecule of CH_4:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (1)$$
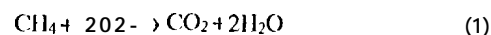
In addition to CH_4 and H_2O, H_2 is the. only other abundant hydrogen-containing species in the stratosphere. Available in situ balloon-borne/rocket measurements of molecular hydrogen in the stratosphere indicate nearly constant mixing ratio with altitude, in accordance with a near balance between production by methane oxidation and loss by oxidation of H_2 (e, g., Ehhalt and Tonnisen, 1980; Brasseur and Solomon, 1986). The primary source of variability of H_2O in the lower stratosphere is related to changes in CH_4, owing to different photolytic histories of individual air masses. Simultaneous observations of H_2O and CH_4 enable us to assess whether changes in H_2O are related to oxidation of CH_4, or some other process. In this paper, recent ATMOS measurements of mixing ratio profiles of H_2O and CH_4 in the height range 16 to 35 km and for a wide. range, of latitudes are examined to test our general understanding of the conservation of H and the hydrogen budget of the lower and middle. stratosphere.

A correlation plot of H_2O vs CH_4 for 47 profiles in the 8-49°N latitude range is shown in Fig. 1. The line represents a linear fit to the measurements (closed symbols) over the 18-35 km range (CH_4 ~ 0.5-1.5 ppmv) given by

$$[H_2O] = (-1.97 \pm 0.04) [CH_4] + 7.18 \pm 0.04 \text{ ppmv} \qquad (2)$$

with the uncertainties representing the standard deviation of the linear regression. The systematic uncertainty in the measurements of H_2O and CH_4 lead to total uncertainties of ± 0.16 and ± 0.43 ppmv in slope and intercept, respectively. The inferred slope $\partial H_2O / \partial CH_4$ ~ -2 implies that each CH_4 molecule is converted into two molecules of H_2O, whereas the intercept 7.18 ± 0.43 indicates the. average total hydrogen H in the 18-35 km region, A precise determination of this slope and its deviation from -2 is important because of its implication for the distribution of H_2 in the stratosphere (Abbas et al., 1996).

Observed mixing ratio of H_2 by balloon-borne instruments suggest a small decrease with height in the 16-35 km range, varying from ~0.55 ppmv at the tropopause to ~0.5 at 30 km (e.g., Ehhalt and Tonnisen, 1980). Assuming conservation of H and H_2, this would correspond to a slope $\partial H_2O / \partial CH_4$ ~ -2.06. Dessler et al. (1994) inferred a value of $\partial H_2O / \partial CH_4$ = -1.94 ± 0.2.7 in the lower

stratosphere from measurements on the ER-2 aircraft. The aircraft, balloon-borne, and ATMOS data in the 16-35 km altitude range are all consistent statistically with conservation of H and with a $\partial H_2O/\partial CH_4$ of '2. The distribution of H with altitude its deviation from a constant value in the upper stratosphere and the mesosphere is discussed in another paper (Abbas et al., 1996).

Measurements of H by other experiments for comparison are: 6.0 ppmv from LIMS and SAMS data (Jones et al., 1986); 7.0 ± 0.6 ppmv at 30 km from the ATMOS experiment on Spacelab 3 (Gunson et al. 1990); 7.6 ± 0.6 ppmv from data collected on the ER-2 aircraft (Dessler et al., 1994). It is unlikely that an atmospheric process could be responsible for the large differences in H observe.d by ATMOS anti the combination of LIMS and SAMS. The Nimbus 7 satellite measurements of H have large systematic errors, as discussed by Hansen and Robinson (1989). A small part crf the difference between values of H measured by the present ATMOS observations and the ATMOS data for April 1985 reported by Gunson et al. (1990) may be accounted for by long term increases in H_2O and CH_4 (Oltmans and Hofmann, 1995; WMO, 1995).

Differences in the determination of H based on the present ATMOS observations and the in situ data reported by Dessler et al, (1994) lie within the systematic uncertainties of both sets of measurements, although the ATMOS value is lower by about 0.4 ppmv. A comparison of ATMOS observations of H_2O, CH_4, and N_2O with nearly coincident in situ measurements obtained in the lower stratosphere during Nov. 1994 shows excellent agreement for each species, yielding virtually identical values of H (Chang et al., 1996). For the Nov. 1994 coincidence, the only available in situ measurements of H_2O and CH_4 were obtained by the NOAA Lyman a hygrometer and the NOAA ACATS (Airborne Chromatograph for Atmospheric Trace Species) gas chromatography, respectively. Dessler et al.'s (1994) estimate of H was based on observations of H_2O and CH_4 from the Harvard Lyman α hygrometer and the ALIAS (Aircraft Laser Infrared Absorption Spectrometer) instrument, respectively. During May 1993 measurements of H_2O by the Harvard hygrometer exceeded those obtained by the NOAA instrument by ~ 15% (Hintsa et al., 1994), and measurements of CH_4 by ALIAS were - 10% lower than measurements by ACATS (Dessler et al., 1994). Consequently, the lower value of H measured by ATMOS relative to the in situ determination of Dessler et al. (1994) may be primarily due to systematic differences in the measurement of H_2O, offset slightly by the differences in observations of CH_4.

The value of H is important for assessing the average. mixing ratio of H_2O injected from the troposphere into the stratosphere. Our estimate. for the. amount of H_2O entering the stratosphere is based on least square fits to ATMOS measurements of H_2O and CH_4 collected over a wide range Of altitudes, rather than observations at the tropopause, to reduce the sensitivity of our result to seasonal and episodic variations in H_2O. ATMOS observations used in the fit were obtained in the 18 to 35 km altitude range, representing an avc.rage. over a period of -18 months, assuming upward velocities of -7 to 8 km per year (see discussion below). Since tropospheric methane is well mixed and has small seasonal variations (~ 3%), we assume a constant mixing ratio of 1.70 ppmv for CH_4 for air entering the stratosphere. This leads to an averaged H_2O mixing ratio of 3.81 ± 0.29 ppmv for air injected into the stratosphere.

Previous in situ and sate.llite observations of this quantity are not in agree.rment: Dessler et al. (1994) determined a value of 4.2 ± 0.5 ppmv from ER-2 data; Hansen and Robinson (1989) reported 3.25

ppmv from LIMS/SAMS data; while Jones et al, (1986) reported 2.7 ppmv from an earlier analysis of the same satellite data. We note again the possibility of large systematic errors that have not been fully quantified in the LIMS/SAMS data (Hansen and Robinson, 1989). The discrepancy between ATMOS and in situ esti mates of H_2O catering the stratosphere lies with the systematic uncertainty of both sets of measurements. The in situ estimate, although based on measurements over the 17 to 20 km altitude range, included a wide range of CH_4 mixing ratios (0.9 to 1.5 ppm) and should have a minor sensitivity to seasonal variations in H_2O. Systematic differences between measurements of H_2O and CH_4 obtained by ATMOS and the in situ observations of Dessler et al. (1994) may be primarily responsible for the offset.

Seasonal Variations in Water Vapor

Since the first detection by Kley c(al. (1 979) of the hygropause, a minimum in the stratospheric water vapor mixing ratio, the nature and mechanism of its formation have been the subject of active discussion in the literature. The amount of water vapor entering the stratosphere may be influenced by temperatures at the tropopause and within' upper troposphere, With the injection limited to the tropical regions, the hygropause altitude was expected to be coincident with the tropopause at tropical latitudes. Numerous measurements have indicated the hygropause to be located above the tropopause by 2 to 3 km (c. g., Russell et al., 1984; Jones et al., 1986; Kelly et al., 1989, 1993). The tropical tropopause has a maximum monthly mean temperature in the summer and occurs at a lower altitude, and has a minimum mean temperature in the winter occurring at a higher altitude (c. g., Reid and Gage, 1981). The variation in tropopause temperature from summer to winter is - 5 K, with a than.gc in altitude of - 1 km. Several recent measurements at tropical latitudes have provide.d convincing evidence of seasonal variations in lower stratospheric water vapor, in phase with changes in annual tropopause temperatures (McCormick, 1993; Hintsa et al., 1994; Boering et al., 1995; Mote et al., 1995).

The simultaneous ATMOS measurements of H_2O and CH_4 rnade during the ATLAS-3 mission in November 1994 are examined for a record of seasonal variations of H_2O entry into the stratosphere. The vertical profiles of H_2O retrieved from a single occultation exhibit periodic. structures of' $\pm$ 3-4% arising from random errors in the retrieval process which may be due to tangent pressure/altitude assignments for the limb-viewing geometry. This structure, however, is largely smoothed out when averaged over a sufficient number of occultations. In addition, there arc systematic differences between the results obtained from the three different optical bandpass filters employed in the observations. To show this variabi lity, we plot in Fig. 2 the profile.s of H_2O retrieved from data obtained during 3-12 November 1994 from three different optical band-pass filters, zonally averaged over: (i) 9 occultations (8-28°N), with filter 3 in the 1580-3340 cm^{-1} region (ii) 4 occultations (9-22°N), with filler 4 in the 3150-4800 cm^{-1} region (iii) 5 Occultations (12-26°N), with filter 9 in the 600-2450 cm^{-1} region (iv) 18 occultations (8-28°N) using data from all filters. The error bars strewn arc the. quadrature sum of the weighted standard deviation of the mean and systematic spectral errors of $\pm$ 6%. The tropopause height indicated in Fig. 2 (and all subsequent figures) is based on an analysis of NMC temperature profiles for the relevant region.

The tropical H_2O profiles exhibit characteristic features with two minima occurring at - 16.5 km and 22.5 km, and two maxima at -

19.0 km and -26.5 km. These features are suggestive of seasonal variations in the H_2O entry into the stratosphere; simultaneous measurements of profiles of CH_4 (not shown) are relative] y featureless, demonstrating that the variability in profiles of H_2O does not originate from oxidation of CH_4. Seasonal variations in lower stratospheric H_2O have also been observed by SAGE II (Rind et al,, 1993), HALOE & MLS (Mote et al., 1995), and instruments aboard the ER-2 aircraft (Boering cl al., 1995). A mid-latitude average profile of H_2O shown in Fig. 3 is relatively featureless, with mixing ratio increasing from a minimum of 4.5 ppmv at the tropopause to about 5.6 ppmv at 35 km. By the time air re.aches tbc mid-latitude region from the tropics, seasonal variations in H_2O are diluted, consistent with the tropical signal largely being overwhelmed by met-idional mixing. Figure 4 shows a comparison of the average H_2O profile of Fig. 2 with the results obtained from near simultaneous observations by the HALOE solar occultation experiment on UARS made during 1-13 November 1994 in the 5"S to 5"N latitude range (Mote et al., 1995), and the NOAA Lyman α hygrometer measurements obtained on ER-2 aircraft on October 29, 1994, from $2.2^{o}S$ to 2.2"N (K. Kelly, private communication). Considering the 0.2 km vertical resolution of the P. R-2 measurements relative to the ATMOS licld-of-view of -1.5 to 2 km, Fig. 4 shows good agree.ment between AI'MOS, HALOE, and in situ measurements of H_2O.

In view of seasonal variations in the water vapor entry into the. stratosphere with a minimum in January and maximum in July (e.g., Rind et al., 1993; Mote et al., 1995), a closc examination of ATMOS profiles of H_2O leads to the following conclusions:

(i) The minimum mixing ratio of H_2O shown in Figs. 2-4 is coincident with the tropopause within the uncertainty of the field-of-view of ATMOS (with the exception of filter 9 measurements), consistent with the phase of the seasonal cycle, i .e., decreasing water vapor entry in November during the observational period; a separation of the. hygropause from the tropopause would be expected in observations obtained after the minimum water vapor entry in January/February to the maximum in June/July , (ii) Assuming the local maximum in the mixing ratio of H_2O at 19 km represents the upward transport of air that entered the stratosphere in July 1994 and the local minimum at 22.5 km reflects entry in January 1994, the inferred vertical velocity is estimated to be -7-8 kn]/year (2.4 x 10^2 cm S-l) near 22 km. This analysis strongly suggests that ATMOS measurements of H_2O and CH_4 are consistent with water vapor entry into the stratosphere in all seasons with a minimum in the winter (January-February) and maximum in the summer (June-Jtrly).

Conclusions

An examination of the simultaneous measurements of H_2O and CH_4 made by ATMOS/ATLAS-3 indicates the near conservation of total hydrogen $H = (H_2O + 2CH_4)$ below altitudes of about 35 km at mid-latitudes. The data indicate that air enters the stratosphere with an average H_2O mixing ratio of - 3.81 ± 0.29 ppmv. Vertical structure in averaged tropical profiles of H_2O suggests seasonal variations in the mixing ratio of H_2O for air entering the stratosphere, and an average velocity of - 7-8 km/year in the lower stratosphere. The hygropause is observed to be within - 2 km of the tropopause at tropical latitudes, and is expected to be above the tropopause only when observed in the January/February to June/July period, when the H_2O content of the air entering the stratosphere reaches its seasonal maximum.

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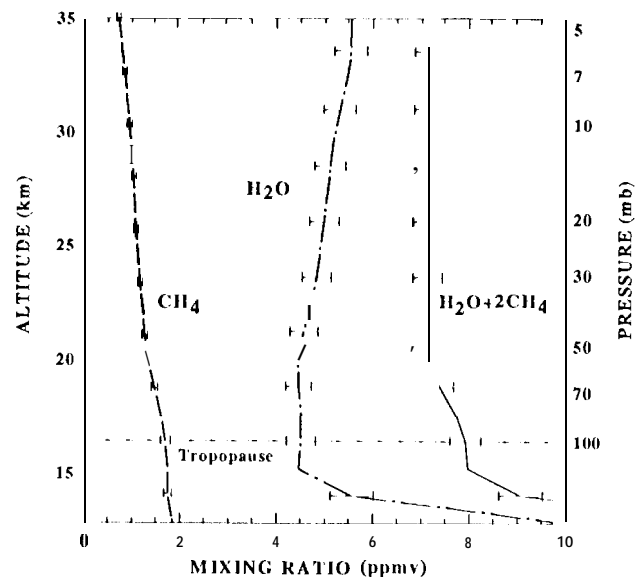J. Geophys.Res., 98, 4835-4856, 1993

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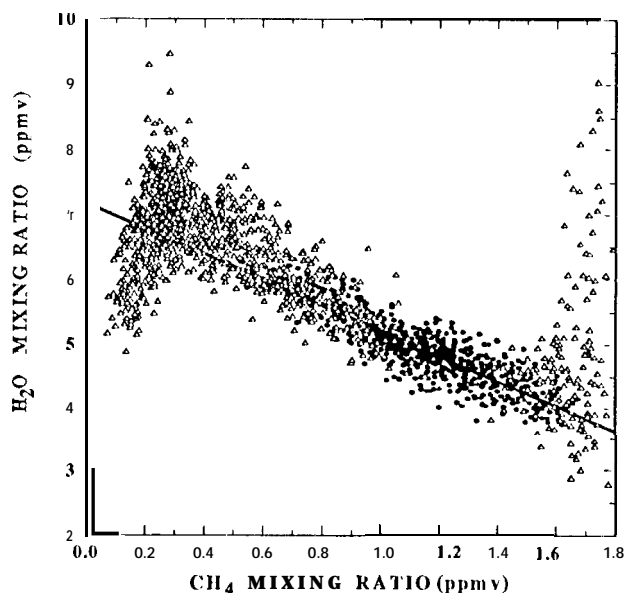
Figure 1. A scatter plot of ATMOS measurements of H_2O vs CH_4 for 47
sunset occultations in the 8-49"N latitude range. The solid line represents
a least square fit (actuations given in text) to data obtained over the 18 to
35 km altitude range (CH_4 - 0.6-1.S ppmv).
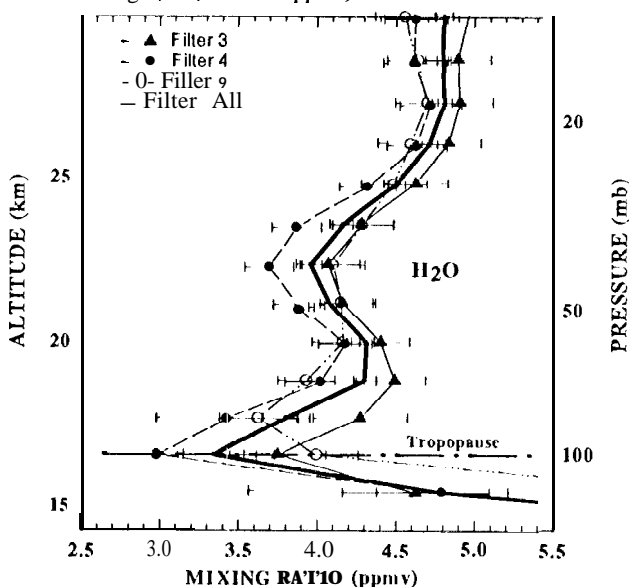
Figure 2. Average profiles of H_2O in the tropics data obtained by
fillers 3, 4, and 9 separately, and an average of profiles obtained
using all filters for latitude range of 8 to 28°N. The tropopause
height, as determined from the National Meteorological Center, is
indicated by tbc horizontal line.

Figure 3. The vertical profiles of CH_4, H_2O, and $H = (H_2O + 2CH_4)$
from a zonal average of 27 sunset occultations for mirt-latitudes in the
latitude 32,-49"N range. The tropopause height, as determined from the
National Meteorological Center, is indicated by the horizontal line.
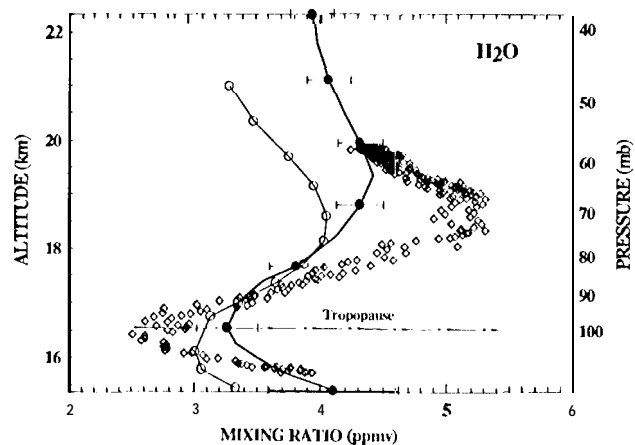
Figure 4. Comparison of the average profile of H_2O retrieved from 18
sunset occultations by ATMOS in the 8-28°N latitude range on November
3-12, 1994 (filled circles) with: NOAA Lyman-a hygrometer
measurements (diamonds) over 2°S-2°N latitudes made on ER-2 aircraft on
October 29, 1994 (K. Kelly, private communication); average of HALOE
measurements (open circles) over 5°S-5°N latitudes made on November
1-13, 1994 (Mote ct al., 1996).